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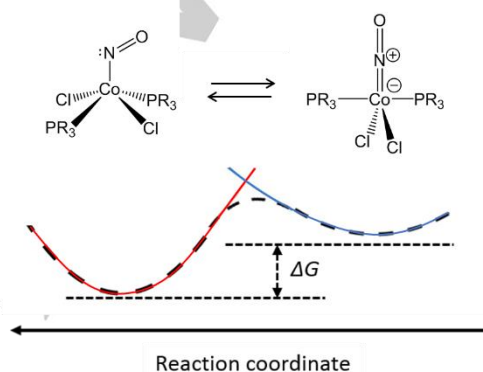
# Spin changes accompany ultrafast structural interconversion in the ground state of a cobalt nitrosyl complex

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**Abstract:** Ultrafast, reversible intersystem crossing (ISC) is reported under ambient conditions for the electronic ground state of the pentacoordinate cobalt nitrosyl complexes,  $[\text{CoX}_2(\text{NO})(\text{PMePh}_2)_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ), in solution. ISC on such short timescales are more typically observed in electronically excited states reached by absorption of ultraviolet or visible light. Singlet and triplet electron spin states of the complex, corresponding to two different isomers, are populated at room temperature, and the two isomers exchange on a timescale of a few picoseconds. Ultrafast two-dimensional infra-red spectroscopy observes the change in wavenumber of the NO ligand band accompanying the isomerization and associated ISC on the (spin) adiabatic ground potential energy surface. Comparison of the dynamics of the chloro- and bromo-complexes shows that inertial effects of the ligand motion have a greater effect than spin-orbit coupling on determining the forward and reverse isomerization and ISC rates.

Intersystem crossing (ISC) between singlet and triplet electron spin states is a common phenomenon in molecules prepared photochemically in electronically excited states by absorption of ultraviolet or visible radiation.<sup>[1]</sup> In contrast, interchange between states of a molecule with different electronic spin under ambient thermal conditions is unusual, because it requires an adiabatic electronic ground state with regions of different spin character connected by a structural change. Here, we investigate the dynamics of spin change in the electronic ground states of cobalt complexes containing a nitrosyl ligand. We use two-dimensional infra-red (2DIR) spectroscopy to observe the rapid (few picosecond) exchange between two isomers which differ in their spin multiplicities. Similar spin dynamics are known for biological structures such as hemoproteins.<sup>[2]</sup> However, the protein architecture restricts these dynamics to the nanosecond to second timescales. The related phenomenon of spin-crossover is widely studied in first-row transition metal complexes, but requires an external stimulus to induce the ISC.<sup>[3]</sup> Two complexes with different halido ligands have been studied,  $[\text{CoCl}_2(\text{NO})(\text{PMePh}_2)_2]$  and  $[\text{CoBr}_2(\text{NO})(\text{PMePh}_2)_2]$ . The isomerization of the chlorido complex is shown in Figure 1. In the approximately square pyramidal (SP) structure, the NO is formally a 1-electron donor with an  $\text{sp}^2$  hybridized nitrogen atom bearing a lone pair of electrons to give a bent Co-N-O linkage. In the approximately trigonal bipyramidal (TBP) isomeric structure, the

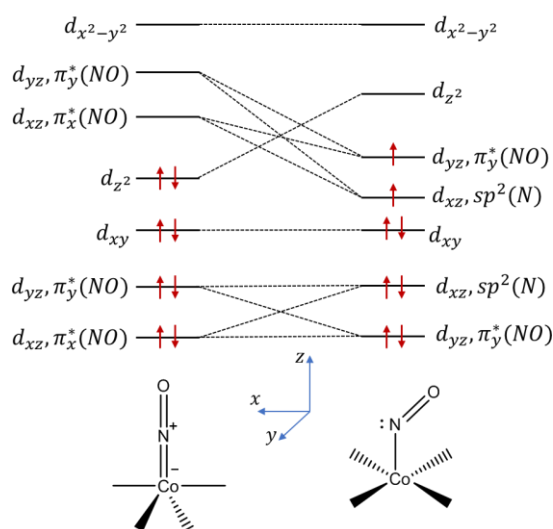
NO is formally a 3-electron donor with an  $\text{sp}$  hybridized nitrogen resulting in a linear Co-N-O arrangement.<sup>[4]</sup> The oxidation states of the Co are nominally +I in the TBP and +III in the SP complexes. Structural isomerization is therefore accompanied by a change in the formal oxidation state of the Co atom, and the isomers are valence tautomers.<sup>[5]</sup>



**Figure 1.** Schematic structures of two isomers of the pentacoordinate  $[\text{CoCl}_2(\text{NO})(\text{PMePh}_2)_2]$  complex and diabatic potential energy curves (red and blue lines) along the isomer exchange coordinate. The dashed black line shows the (spin) adiabatic ground state potential energy surface.

Figure 2 shows molecular orbital (MO) diagrams for 5-coordinate cobalt nitrosyl complexes with four identical ligands.<sup>[4]</sup> The TBP and SP geometries are associated with singlet and triplet states respectively. In the SP complex, the  $\{d_{yz}, \pi_y^*(\text{NO})\}$  orbital is stabilized through interactions with the other ligands, bringing it close enough in energy to the  $\{d_{xz}, \text{sp}^2(\text{N})\}$  MO that a triplet spin-state becomes the ground electronic configuration.<sup>[6]</sup> The existence of a paramagnetic compound is supported by magnetic susceptibility and  $^{31}\text{P}\{-^1\text{H}\}$  NMR signal broadening measurements described in Supporting Information (SI). The different electronic characters of the two structures require the exchange dynamics to be described by an adiabatic ground-state potential energy surface (PES) constructed from diabatic PESs for the TBP and SP isomers (Figure 1).

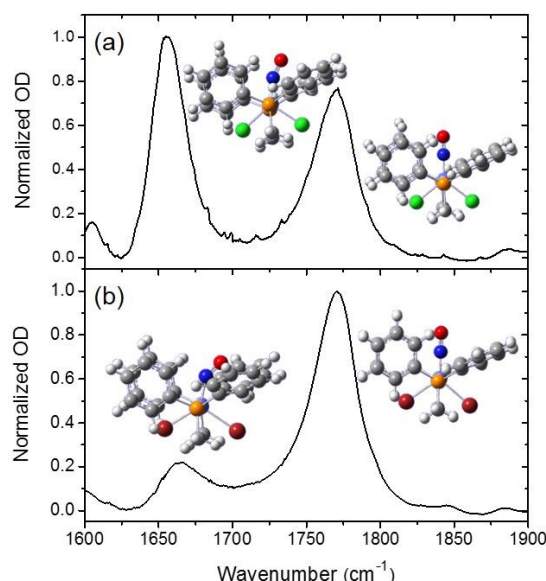
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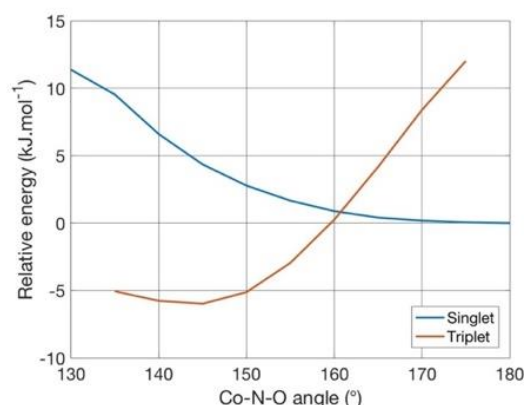
**Figure 2.** Molecular orbital diagram of a pentacoordinated cobalt nitrosyl complex adopting either a TBP (left) or SP (right) structure. The figure is adapted from ref. [4].

Most cobalt nitrosyl complexes adopt either the bent Co-N-O (triplet)<sup>[6-7]</sup> or linear Co-N-O (singlet)<sup>[8]</sup> structures at thermal equilibrium,<sup>[8]</sup> but in selected cases the two geometries are close enough in energy that both are accessible at ambient temperature.<sup>[6, 9]</sup> The chosen complexes are such examples. Steady state IR absorption spectroscopy in the N-O stretching region differentiates between the two forms of the complex, with the NO band of the triplet complex shifted to lower wavenumber because greater localization of the  $\pi^*$  electron density on the nitrosyl ligand gives double-bonded NO<sup>-</sup> character.<sup>[10]</sup> Figure 3 shows an FTIR spectrum of a dichloromethane (DCM) solution of [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>]. The peaks at 1655 and 1765 cm<sup>-1</sup> are respectively assigned to the triplet and singlet forms.<sup>[9b]</sup> In time-dependent 2DIR spectra reported below, isomeric exchange gives rise to characteristic off-diagonal (cross) peaks from which the kinetics of exchange can be deduced.<sup>[11]</sup>

The computationally optimized geometries for the singlet and triplet states of [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] are shown in Figure 3. Computational methods are described in the SI. In the singlet (distorted TBP) state, the Co-N-O angle is 180° and the Cl-Co-Cl angle is 103°. The corresponding optimized geometry for the triplet complex contains a bent nitrosyl coordination with a Co-N-O angle of 144° and a Cl-Co-Cl angle of 114°. The computed intensities for the two isomer N-O bands are similar, being 506 and 533 km mol<sup>-1</sup> for the singlet and triplet respectively. Hence IR intensities in **Figure 3** can be directly related to relative abundances. Single crystal X-ray diffraction structures of both the [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] and [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] complexes support the co-existence of the two isomers (see SI).



**Figure 3.** FTIR spectra of DCM solutions of a) [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] and b) [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] in the NO stretching region. Band assignments to the two isomeric forms are shown by the computed structures.



**Figure 4.** Relaxed energy scans of the Co-N-O angle on the triplet (red) and singlet (blue) electronic states.

Relaxed scans of the Co-N-O angle were conducted from the two electronic state minima while optimizing all the other molecular degrees of freedom and maintaining the overall spin character of the complex. The obtained potential energy profiles are plotted in Figure 4. The triplet state minimum is computed to lie 6.0 kJ mol<sup>-1</sup> lower in electronic energy than the singlet minimum, corresponding to a Boltzmann population of 92% in the triplet and 8% in the singlet state. The calculations were performed for a gas-phase environment, but are supported by the FTIR spectrum of [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] in cyclohexane, a weakly interacting solvent, which indicates a similar population ratio (see SI, Figure S2).

	[CoCl <sub>2</sub> (NO)(PMePh <sub>2</sub> ) <sub>2</sub> ]		[CoBr <sub>2</sub> (NO)(PMePh <sub>2</sub> ) <sub>2</sub> ]	
	Singlet	Triplet	Singlet	Triplet
Vibrational lifetime	50.2 ± 6.9 ps	17.6 ± 0.4 ps	37.3 ± 1.1 ps	18.0 ± 0.5 ps
Orientalional time constant	239 ± 21 ps	507 ± 20 ps	117 ± 12 ps	103 ± 14 ps
Exchange time constant	Singlet → Triplet		Singlet → Triplet	
	8.8 ± 1.0 ps		31.0 ± 6.2 ps	
	Singlet ← Triplet		Singlet ← Triplet	
	11.6 ± 2.3 ps		12.9 ± 2.6 ps	

**Table 1:** Exchange, vibrational relaxation and orientational decay time constants for [CoX<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] (X = Cl, Br) complexes in dichloromethane.

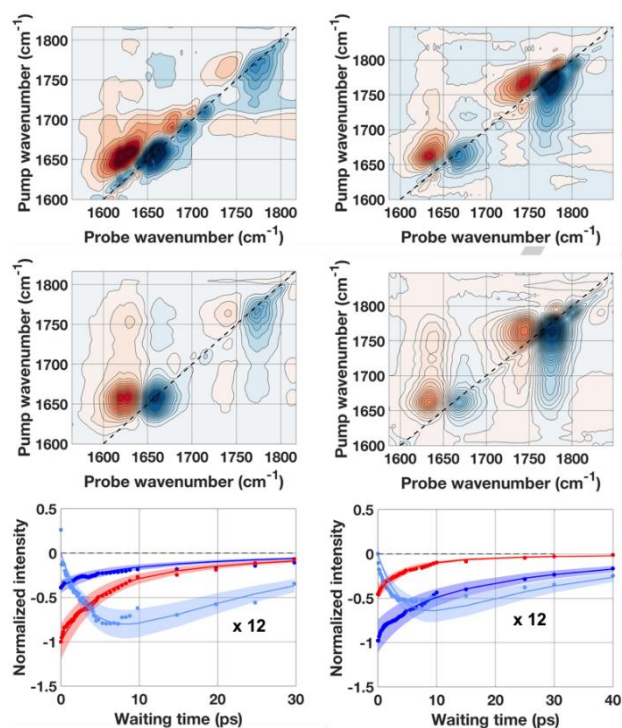
2DIR spectra of [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] and [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] in DCM are shown in Figure 5 for early and later waiting times (see SI for methods). The former spectrum contains additional diagonal features at 1690, 1711 cm<sup>-1</sup>, and as a shoulder on the peak at 1793 cm<sup>-1</sup> which originate from air reaction products. They are particularly evident in the T<sub>w</sub> = 300 fs spectrum because this was one of the last spectral time-points acquired. The effect on extracted exchange kinetics from growth of these impurities was minimized by randomizing the waiting time delays during data collection.

The off-diagonal peaks grow with increasing waiting time, indicating exchange between cobalt nitrosyl isomers. Vibrational relaxation and orientational diffusion cause a slower decay. The kinetic data for [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] were simultaneously fitted with a model which incorporated these factors (see SI).<sup>[12]</sup> Four fitting parameters, the exchange coefficients and the transition dipole moments of the two isomers, were adjusted. The obtained fits are shown in Figure 5 as solid lines, and Table 1 reports the derived time constants. A similar analysis was undertaken for the [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] complexes, for which the air degradation product features appear on the diagonal at 1700, 1720 and 1800 cm<sup>-1</sup>.

Equilibrium constants, calculated from the ratio of the exchange rate coefficients, are  $K_{\text{Singlet/Triplet}} = 0.75 \pm 0.30$  for [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] and  $K_{\text{Singlet/Triplet}} = 2.4 \pm 0.9$  for [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>]. The corresponding estimates from band intensities in the FTIR spectra are 0.77 and 4.2. These latter estimates assume equal transition dipole moments for the two isomers, consistent with the outcomes of our electronic structure calculations. Using the detailed balance relation for the equilibrium, the changes in Gibbs free energy between the triplet and singlet species in CH<sub>2</sub>Cl<sub>2</sub> solution are evaluated as  $0.7 \pm 0.3$  and  $-2.1 \pm 0.8$  kJ mol<sup>-1</sup> for [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] and [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>], respectively. The triplet minimum is lower in energy in [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] and the singlet minimum is lower in [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>].

The rates of interconversion of the two isomers could be controlled by either the nuclear dynamics, or the coupling between singlet and triplet spin states. The heavier bromine atoms should slow down the exchange dynamics through inertial effects, but the greater spin-orbit coupling of the heavier halogen atoms (with spin-orbit coupling constants of -176 cm<sup>-1</sup> for Co, -587 cm<sup>-1</sup> for Cl and -2456 cm<sup>-1</sup> for Br<sup>[13]</sup>) is expected to enhance the mixing of singlet and triplet states in regions of near degeneracy. The larger time constant obtained for ISC from the higher to lower energy isomer in [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] than in [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] indicates that the inertial effect of the heavier halogen ligands is the more important factor.

The observed changes in spin multiplicity in a pentacoordinate cobalt nitrosyl complex are driven by environmental fluctuations, and occur reversibly on timescales of a few picoseconds. The precise evidence derived from our 2DIR measurements should provide useful insights for the behaviour of cobalt nitrosyl complexes in biological systems, and for spin-crossover dynamics.



**Figure 5.** 2DIR spectra of [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] (left column) and [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] (right column) in DCM at early waiting times (T<sub>w</sub> = 300 fs – top row) and averaged over intermediate waiting times (middle row; T<sub>w</sub> = 2800 to 4500 fs for [CoCl<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>] and T<sub>w</sub> = 3600 to 8500 fs for [CoBr<sub>2</sub>(NO)(PMePh<sub>2</sub>)<sub>2</sub>]) to highlight weak cross peaks. Negative going features are shown in blue, and positive features in red. The black dotted lines indicate the diagonals. The bottom row shows time dependences of bleach spectral features extracted from the 2DIR spectra by integration of band intensities at each waiting time (filled circles) and fits to a kinetic model (solid lines). Shaded regions correspond to 20% confidence intervals. The regions integrated are shown by the coloured boxes in the spectra. The cross-peak intensities have been multiplied by a factor of 12.



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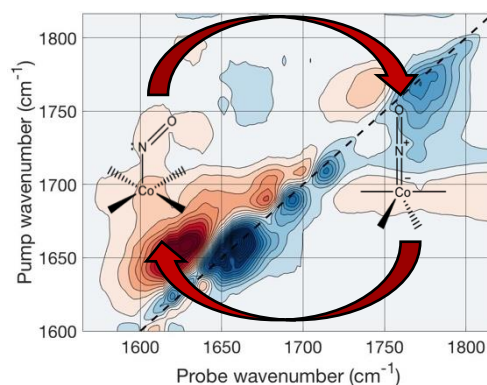
All experimental data are archived in the University of Bristol's Research Data Storage Facility (DOI 10.5523/bris.3g7165svhjw82im34mlpinzpm).

**Keywords:** Intersystem crossing, Ultrafast dynamics, Two-dimensional Infrared Spectroscopy.

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## COMMUNICATION

The ground state intersystem crossing of a cobalt nitrosyl complex is shown to occur on an ultrafast time scale. The electron spin changing dynamics are observed using two-dimensional infrared spectroscopy by probing the nuclear vibrational frequencies associated with each electronic state. Comparison of the spin-state exchange rates in two halido substituted complexes shows that inertial effects outweigh ligand spin-orbit coupling effects.



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